CMCS Highlight: Active Thermochemical Tables

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January, 2003

ATcT Web Service Demonstrated in CMCS Portal

The development of the first version of Active Thermochemical Tables (ATcT) and the successful demonstration of this application within the Collaboratory for Multi-scale Chemical Science (CMCS) Web-based portal are significant steps towards the CMCS goal to enhance chemical science. ATcT are a novel scientific application, centered on a distinctively different paradigm of how to obtain reliable thermochemistry. As opposed to conventional thermochemical tables, which are based on sequentially developing thermochemical values for the chemical species of interest, Active Thermochemical Tables are based on the thermochemical network approach.[1,2] Several successful presentations and demonstrations of ATcT and its integration have been conducted, including at Supercomputing 2002 and Grid2002. The broad availability of the ATcT approach and data products promises a new paradigm in the chemical science community with rapidly accessible, accurate, reliable, and self-consistent thermochemistry data. This data is crucial in kinetics and chemical mechanism research, in predictive modeling of chemical systems, and in many industrial applications.

ATcT web services were demonstrated as a use case for a kineticist who is seeking thermochemical data for methyl peroxy radial (CH_3OO) in the context of investigations

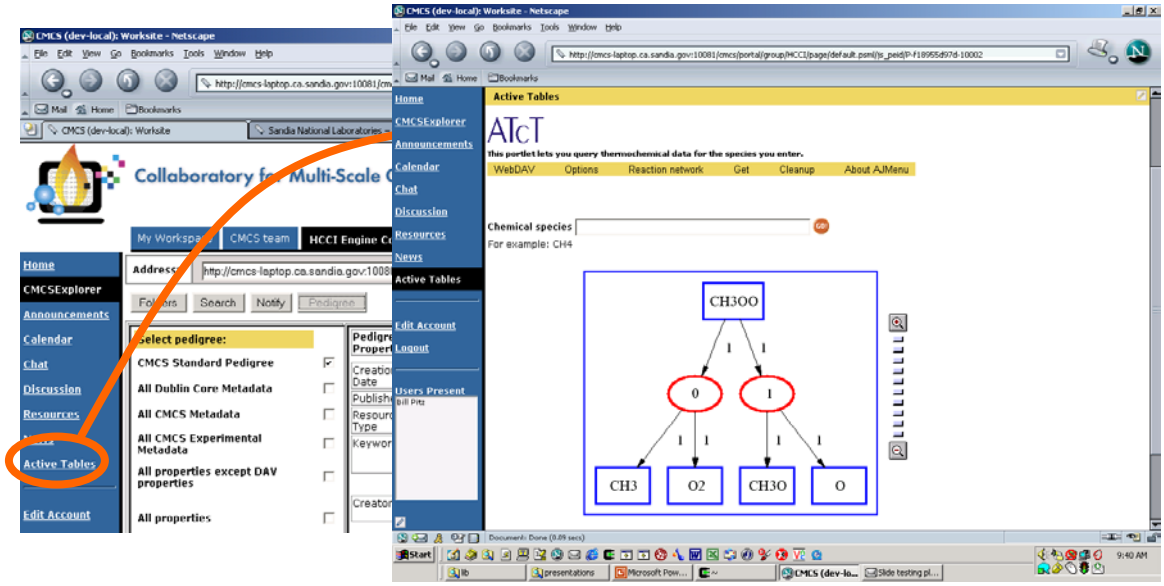

Figure 1. The Active Tables (ATcT) Web service is available from the HCCI Project Team workspace in the CMCS Portal (shown from view of pedigree of computational data used provide new inputs into Active Tables).

of combustion modeling in a Homogeneous Charge Compression Ignition (HCCI) engine. A search within the CMCS portal reveals recent high-quality calculations that provide needed bond energies. The CH_3OO dataset is integrated it into his workspace of ATcT thermochemistry tables, established in earlier work and stored in his CMCS workspace. As shown in Fig. 1, the kineticist activates the ATcT portlet by clicking on

Active Tables capability shown on the left bar of his HCCI team workspace. He imports his updated ATcT data into the Active Tables service. He is then able to run the Active Tables optimization that produces a state-of-the-art value for the enthalpy of formation of methyl peroxy radical. The resulting thermochemical network displayed by ATcT is shown in Fig. 1. Then he can export to CMCS an optimized table of thermochemistry data for methyl peroxy. The exported data automatically inherit the Active Table's pedigree, including new pedigree information provided by the kineticist, namely, the reference to the calculation.

Additional features of the demonstration included an automatically generated translation (*via* CMCS middleware) of the new Active Tables data from XML into the commonly used JANAF format and some resulting automatic operations. Additional features of the demonstration included automatically generated translations of the new ATcT data. An event generated by the appearance ATcT data in the CMCS repository triggers automated creation of derived data sets including a 'NASA5' polynomial fit to the data, which is required by common combustion kinetics modeling software, and tabular data that can be visualized within the CMCS portal to assess the quality of the fit to the ATcT data.

Active Tables development

ATcT has several functional parts: the computational kernel, the underlying libraries defining the thermochemical network, a user interface, and a Web services framework. The ATcT kernel is quite complex. The 1.0 Beta release has nearly 40,000 lines of Fortran 95 code. The developed capabilities include a several approaches to calculate the partition function for the chemical species of interest and a simultaneous solution of the network via χ^2 minimization, resulting in a set of preferred thermochemical values for the chemical species involved. It also includes a large set of user-selectable options (for example, which ATcT libraries to access and a selection of output data parameters such as temperature schedule, output units, etc.), as well as internal versioning of data contained within the ATcT libraries. During the demonstrations, the released version performed flawlessly, exactly as designed and expected.

The underlying data needed by ATcT is organized in a number of Libraries and Notes. Libraries are large collections of data, typically generated by thermochemical committees who oversee and anoint the scientific soundness of the content. Notes are lighter versions of Libraries, typically associated with individual users or collaborative workgroups. Another library (JANAF Library) contains a large number of species from the popular JANAF[3] tabulation (almost all of its gas-phase species). The Gurvich Library contains a similar (albeit smaller) set of tabulated enthalpies extracted from the popular Russian tabulation of Gurvich et al.[4] Similarly, a slightly smaller library contains a tabulation of CODATA-recommended[5] selected enthalpies of key chemical species. In addition, a small library (Pitz Notes) that contains a selection of networked data (relating to methyl-peroxy radical) that were directly used in the demonstrations was also assembled.

Also developed were the ATcT GUI and the infrastructure aspects of the distributed architecture that were needed to efficiently interface the ATcT kernel with the CMCS infrastructure. An integral part of this architecture is the exposure of the complex ATcT Fortran program through sophisticated, possibly distributed, Web services. These services allow easier integration within a collaborative framework as anticipated within the

overall SciDAC project goals. The necessary interfaces were developed as part of this service. Among others, these allow the transformation of data needed and produced by the native ATcT component to an XML format that can be reused with ease within the rest of the CMCS framework.

As the development of the services is independent of the presentation technology, the access mechanism to the functionality of the ATcT program has been provided through a web portal. Related portlets were developed to provide a menu allowing the user of the Active Thermochemical Table component to access suitable tasks such as displaying a graph of chemical reactions or querying thermochemical data on a chemical species.

Some of the technologies used within this project have been developed and explored as part of other projects, including the DOE SciDAC CoG Kit project and its interactions with the NSF Alliance Portal Expedition, and CHEF (CompreHensive collaborativE Framework, U. Mich). Additional collaborative contributions occurred through the SAM (Scientific Annotation Middleware project, DOE NC program) project and a variety of open source technologies, some of which are listed in CMCS Portal Infrastructure Highlight.

Some Scientific Ramifications of the current ATcT development

Ruscic et al.[6,7] have recently convincingly shown that the generally accepted bond dissociation energy in water is too high by ~2 kJ mol^{-1} and proposed its revision. This study left open a small discrepancy of ~20 cm^{-1} = 0.2 kJ mol^{-1} between the photoionization measurements and the value obtained by Rydberg-tagging techniques. Subsequently, Ruscic et al.[8] have addressed the resolution of this remaining small discrepancy by using the present network approach (in a "manual" mode at the time). The network approach shows convincingly that the Rydberg tagging result is slightly off. While the final result of the analysis of this problem via ATcT is no different than the initial "manual" approach, its implementation through ATcT is clearly more elegant and substantially more efficient, making the "manual" approach obsolescent.

Additionally, the process of construction of the critically-evaluated networked data in the Main Library and its interim harmonizations and solutions is not only providing new and improved thermochemical quantities for several very basic ("key") chemical species, but also providing pointers to future experimental measurements that will "tighten" the network and bring improvements to the derived thermochemistry (one good example is the planned re-examination of ozone via photoionization).

Publications and references

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